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(54) Surfactant compositions.

(57) Disclosed are novel low skin irritation surfactant compositions which are high in foaming properties containing, as active ingredients, a diamine monoalkyl phosphate salt and an alkylamine oxide.

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TECHNICAL FIELD

The present invention relates to novel low skin irritation surfactant compositions which are high in foaming properties containing, as active ingredients, a diamine monoalkyl phosphate salt and an alkylamine oxide.

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BACKGROUND OF THE INVENTION

Soaps, detergents and abrasives have long been used to cleanse the skin on various portions of the body. Anionic surfactants such as alkyl sulfates, polyoxyethylene alkyl sulfates, alkylbenzene sulfonates and α -olefin sulfonates have been widely used as the surfactant component for many cleansers.

It is known that such anionic surfactants are adsorbed and thereby remain on the skin surface to cause dryness and scaling of the epidermis, or skin chapping and roughness, if they are used continually. Thus, skin troubles such as roughness of hands are apt to be caused by the use of detergents. Skin roughness can be a precursor of more severe skin troubles such as eczema. Thus, there is an urgent need to eliminate this disadvantage.

Nonionic surfactants, on the other hand, cause little or no skin dryness or roughness. However, they do not have the same advantageous properties of foaming and detergency as anionic surfactants. It has, therefore, not been suitable to incorporate nonionic surfactants into cleansing compositions as the primary detergent component.

Phosphoric acid esters have been known as anionic surfactants, generally as mono- and diesters, or mixtures thereof. However, in general, their water solubilities and foaming properties are not very good.

European Patent No. 265 702 published May 4, 1988 discloses transparent or semi-transparent cosmetic compositions containing a monoalkyl phosphate, water, oil and alcohol for skin treatment. The oils and alcohols are used to obtain clarity. U.S. Patent 4,573,749 to McIntosh, issued June 28, 1988 discloses monoamine alkyl phosphates having antimicrobial activity. U.S. Patent 4,290,904 to Popper et al., issued September 22, 1981, U.K. Patent No. 1,513,053, published June 7, 1978 and European Patent 023 978, published February 18, 1981 disclose cosmetic and toiletry preparations containing alkoxylated alkylene diamines. U.S. Patent 4,476,043, 4,476,044 and 4,476,045 to O'Lenick, all issued October 9, 1984 and U.S. Patent 4,477,372 to O'Lenick, issued October 16, 1984 disclose substantially non-aqueous surfactants containing an organic sulfate, mineral oil and an alkoxylated amine. However, none of these references disclose the use of a diamine alkyl phosphate surfactant alone or in combination with an amine oxide.

Monoalkyl phosphate salts have also been disclosed as useful surfactants in U.S. Patent 4,139,485 to Imokawa et al., issued February 13, 1979. However, these surfactants form turbid aqueous solutions unless they contain other solvents (e.g., solubilizing agents). Further, the rheology of these salts limits the variety of formulations which can be made with aesthetically pleasing characteristics.

It has been discovered that certain novel transparent and stable surfactant compositions containing diamine monoalkyl phosphate salts and alkylamine oxides readily enable the preparation of stable non-presurized, aerated foams. These foams possess good cleansing power and detergency, are mild and non-irritating, and leave little, if any, residual film remaining on the cleansed surface of the skin. These compositions are homogeneous in nature, can be structured to be wet or dry, stable or fastbreaking, and are aesthetically suitable for use in a wide variety of personal care products.

One of the principal purposes of this invention is to describe the preparation of an aqueous skin cleansing composition which will produce a usable foam from a hand-held, squeezable foam dispensing device, as well as from an aerosol device and further which will not render the device unusable by, for example, clogging the device.

Another object of this invention is to provide surfactant compositions which produce relatively stable or collapsible foams. A preferred embodiment of this invention is to provide skin cleansing foams of low density.

Another object of this invention is to provide surfactant compositions with creamy lather, good skin feel and good rinsability and which retains skin elasticity.

Another object of this invention is to provide surfactant compositions which are mild and non-irritating to skin and eyes and which do not require the use of propellants, thereby avoiding the danger of explosion or corrosion of the container.

Still another object of this invention is to provide a foam producing composition such that if placed in a hand-held, foam dispensing device having deformable walls, the amount of force required to produce the foam is not excessive (i.e., less than about 15 psi) and is readily usable by the average person.

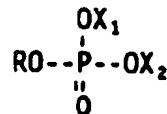
These objectives as well as others apparent to those skilled in the art are obtained with the compositions described herein.

SUMMARY OF THE INVENTION

This invention comprises surfactant compositions comprising:

(a) from about 0.1% to about 99.0% of one or more of a surfactant compound of the formula:

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wherein R is a hydrophobic group or the condensation product of a hydrophobic group with ethylene oxide, preferably R is alkyl or alkenyl having an average of from about 10 to 18 carbon atoms, and wherein X₁ and X₂ are independently selected from the group consisting of hydrogen, alkali metal, ammonium, substituted ammonium (e.g., alkoxyLATED ammonium, alkylammonium, alkoxyLATED aliphatic amines, polyethoxylated amines) and alkylene diamine, provided that at least one of X₁ and X₂ is an alkylene diamine; and

(b) from about 0.1% to about 20.0% of an alkylamine oxide which has a hydrocarbon group having from about 10 to about 14 carbon atoms.

Sesquialkyl phosphate salts are not within the scope of the present invention.

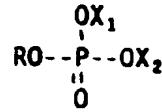
All parts, percentages and ratios used herein are by weight and all measurements are at 25°C unless otherwise indicated.

DETAILED DESCRIPTION OF THE INVENTION

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The surfactants of the present invention are certain diamine monoalkyl phosphate salts of the formula:

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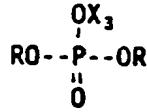


wherein R is a hydrophobic group or the condensation product of a hydrophobic group with ethylene oxide, preferably R is alkyl or alkenyl having an average of from about 10 to 18 carbon atoms, and wherein X₁ and X₂ are independently selected from the group consisting of hydrogen, alkali metal, ammonium, substituted ammonium (e.g., alkoxyLATED ammonium, alkylammonium, alkoxyLATED aliphatic amines, polyethoxylated amines) and alkylene diamine, provided that at least one of X₁ and X₂ is an alkylene diamine. Preferably, R is the condensation product of a hydrophobic group with from about 1 to about 10 moles and preferably from about 1 to about 4 moles of ethylene oxide.

Preferred compositions comprise a mixture of the diamine monoalkyl phosphate salts wherein R is selected from the group consisting of C₁₂ to C₁₄ alkyl or alkenyl and C₁₆ to C₁₈ alkyl or alkenyl (or the condensation product of these moieties with ethylene oxide) and wherein said salts are present in a ratio of from about 80:20 to about 20:80, preferably from about 60:40 to about 40:60 and most preferably from about 55:45 to about 45:55, respectively.

These monoalkyl phosphate salts can be prepared, for example, by a known process wherein a long chain aliphatic alcohol is reacted with a phosphatizing agent such as phosphoric anhydride or phosphorus oxychloride. It is recognized that the dialkyl phosphate can be by-produced by this process and which possess poor water-solubility or foaming properties. Such dialkyl phosphates have the formula:

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wherein R is a hydrophobic group or the condensation product of a hydrophobic group with ethylene oxide, preferably R is alkyl or alkenyl having an average of from about 10 to 18 carbon atoms, and wherein X₃ is selected from the group consisting of hydrogen, alkali metal, ammonium, substituted ammonium (e.g., alkoxyLATED ammonium, alkylammonium, alkoxyLATED aliphatic amines, polyethoxylated amines) and alkylene diamine.

Preferably, the weight ratio of the diamine monoalkyl phosphate salt to the dialkyl phosphate salt is from about 99:1 to about 70:30, respectively, preferably from about 100:0 to about 90:10, most preferred is a ratio of substantially 100:0. However, unlike monoamine, alkali or ammonium phosphate salts, these diamine phosphates of the diester are uniquely water-soluble and, therefore, will not interfere as much with the devices and formulations described herein.

These surfactants are particularly useful in detergent products which are directly contacted with the skin for a long time such as facial cleansers, shampoos, and solid synthetic detergent toilet bars, because they have a characteristic, excellent foaming power and skin roughness is not caused. The surfactants can also be used as ingredients of dish-washing liquid detergents, powder detergents and dentifrices and are particularly useful compositions where a clear and non-turbid surfactant is desirable.

The saturated and unsaturated hydrocarbon groups having an average carbon number of 10-18 (R) are straight chain, branched or alicyclic hydrocarbons such as decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups and corresponding olefinically unsaturated groups. Those hydrocarbon groups are contained in the compositions singly or in the form of a combination of several groups. Saturated hydrocarbon groups of an average carbon number of 10 to 14 and unsaturated hydrocarbon groups of an average carbon number of 16 are particularly preferred. Also preferred for use herein are the saturated or unsaturated hydrocarbon groups wherein said hydrocarbon groups possess from about 1 to about 10 units and preferably from about 1 to about 4 units of ethylene oxide per molecule.

The preferred alkali metals for X₁ and X₂ according to the invention, are, for example, lithium, sodium and potassium.

The alkylammonium or substituted alkylammonium for X₁ and X₂ according to the invention, are cations produced from amines used for neutralization of the corresponding phosphoric acids by salt formation after the neutralization step in the process for preparing monoalkyl phosphate salts in the present invention. The corresponding amines are primary, secondary and tertiary amines having alkyl groups of 1 to 4 carbon atoms which can be further substituted, particularly by hydroxyl groups. As the amines, there can be mentioned, for example, dimethylmonoethanolamine, methyldiethanolamine, trimethylamine, triethylamine, dibutylamine, butyl-dimethylamine, monoethanolamine, diethanolamine, triethanolamine, isopropylidimethylamine and isopropylethanolamine. Preferred amines are monoethanolamine, diethanolamine and triethanolamine. A particularly preferred amine is triethanolamine. Other useful amines include arginine, lysine, mono-, di- or triisopropanolamine, N,N-tris(hydroxymethyl)aminomethane, diglycolamine, glucamine, aminomethylpropanol, and aminomethylpropanediol. Also useful in the present invention are the copolymers derived from the addition of ethylene oxide and propylene oxide available as Tetronic® and Tetronic R® available from BASF Corporation and the polyethoxylated amines available as the Ethomeen® series available from Armak Corporation.

The alkylene diamine, according to the present invention has the general formula:

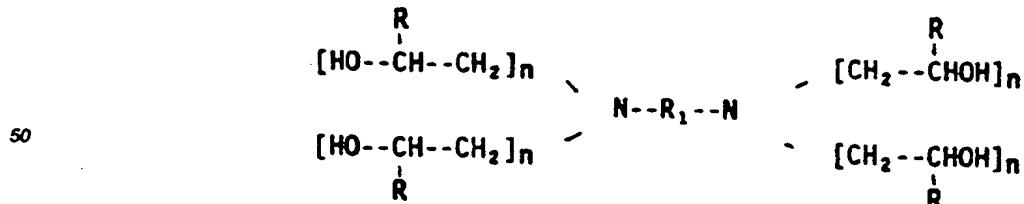


in which R₁, R₂, R₄ and R₆ are independently hydrogen, an alkyl group having 1 to 4 carbon atoms or a hydroxylalkyl or dihydroxyalkyl group having 1 to 4 carbon atoms or R₄ and R₆ jointly form a saturated 5 or 6 membered heterocyclic ring, which can be substituted by an oxo- or hydroxylalkyl group and R₃ represents an alkylene or hydroxyalkylene group having 2 to 4 carbon atoms, provided that at least one of R₁, R₂, R₃, R₄ and R₆ contain at least one hydroxy group.

These compounds are fully disclosed in U.K. Patent 1,513,053, published June 7, 1978.

A particular amine class that is useful herein is an N,N-tetrakis (hydroxylalkyl) ethylene diamine having the formula:

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wherein R₁ is alkylene having two to four carbon atoms, R is hydrogen or an alkyl group having one to six carbon atoms and n is from one to four. The foregoing diamine preferably has a molecular weight of under about 1700, preferably under about 1200, even more preferably under about 800 and most preferably under about 500.

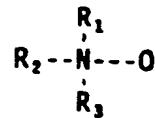
Although other examples will also be given hereinafter, the tetrakis (hydroxylalkyl) ethylene diamine is best exemplified by the compound N,N,N',N'-tetrakis(2-hydroxypropyl)-ethyl nediamine, obtainable commercially

under the trademark Quadrol or Neutrol TE (both available from BASF Wyandotte Company).

Examples of diamine monoalkyl phosphate salts useful in the present invention include, but are not limited to,

- 5 tetrahydroxypropylethylenediamine monococoylphosphate,
- tetrahydroxypropylethylenediamine monolaurylphosphat ,
- tetrahydroxypropylethylenediamine (monoethoxylated) monolaurylphosphate,
- tetrahydroxypropylethylenediamine monoisostearylphosphate,
- tetrahydroxypropylethylenediamine monostearylphosphate,
- 10 tetrahydroxypropylethylenediamine (monoethoxylated) monostearylphosphate,
- tetrahydroxypropylethylenediamine monomyristylphosphate,
- tetrahydroxypropylethylenediamine (monoethoxylated) monomyristylphosphate,
- tetrahydroxypropylethylenediamine monooleylphosphate,
- 15 tetrahydroxypropylethylenediamine monopalmitylphosphate,
- tetrahydroxypropylethylenediamine (monoethoxylated) monopalmitylphosphate,
- tetrahydroxypropylethylenediamine monocaprylphosphate,
- tetrahydroxypropylethylenediamine (monoethoxylated) monocaprylphosphate,
- tetrahydroxypropylethylenediamine monoundecylenylphosphate,
- tetrahydroxypropylethylenediamine monotridecylénylphosphate,
- 20 tetrahydroxypropylethylenediamine mono(methylmyristyl)phosphate,
- tetrahydroxypropylethylenediamine mono(isopropylauryl)phosphate,
- tetrahydroxypropylethylenediamine mono(isodecyneopentyl)phosphate,
- tetrahydroxypropylethylenediamine monocetylphosphate, and
- tetrahydroxypropylethylenediamine mono(isopropylmyristyl)phosphate.

The alkylamine oxides of the present invention have a hydrocarbon group having from about 10 to about 25 carbon atoms. The alkylamine oxides can be represented, for example, by the following general formula:



30 wherein R_1 is a hydrocarbon group having about 10 to about 14 carbon atoms and R_2 and R_3 are independently a methyl or ethyl group.

The compositions of the present invention can be administered topically, i.e., by the direct laying on or spreading of the composition on epidermal or epithelial tissue. Such compositions can be formulated as foams, lotions, creams, ointments, solutions, gels or solids. A highly preferred composition contains the monoalkyl phosphate salt in a soap matrix (i.e., liquid or solid). These topical compositions comprise a safe and effective amount, usually from about 0.1% to about 99.0%, and preferably from about 1% to about 10%, of the monoalkyl phosphate salt and from about 0.1% to about 20.0% of the alkylamine oxide. Bar compositions generally contain very high levels i.e., above 80%, of the diamine monoalkyl phosphate salt. Generally, the carrier is either organic in nature or a solution or an aqueous emulsion and is capable of having the active components dispersed, dissolved or suspended therein. The carrier can include pharmaceutically-acceptable emollients, skin penetration enhancers, coloring agents, fragrances, emulsifiers, thickening agents, and solvents. A more detailed description of such forms follows:

45 1. Lotions.

The lotions can comprise a safe and effective amount of the monoalkyl phosphate salt and the alkylamine oxide; from about 0.1% to about 25%, preferably from about 3% to about 15%, of an emollient; the balance being water, a C_2 or C_3 alcohol, or a mixture of water and the alcohol. Examples of suitable emollients are as follows:

- 50 1. Hydrocarbon oils and waxes. Examples are mineral oil, petrolatum, paraffin, ceresin, ozokerite, micro-crystallin wax, polyethylene, and perhydrosqualane.
- 2. Silicone oils, such as polydimethylsiloxanes, methylphenylpolysiloxanes, water-soluble and alcohol-soluble silicone-glycol copolymers.
- 55 3. Triglyceride fats and oils, such as those derived from vegetable, animal and marine sources. Examples include castor oil, safflower oil, cotton seed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, and soybean oil.

4. Acetoglyceride esters, such as acetylated monoglycerides.
5. Ethoxylated glycerides, such as ethoxylated glyceryl monostearate.
6. Alkyl esters of fatty acids having 10 to 20 carbon atoms. Methyl, isopropyl and butyl esters of fatty acids are especially useful herein. Examples include hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, lauryl lactate, myristyl lactate, and cetyl lactate.
7. Alkenyl esters of fatty acids having 10 to 20 carbon atoms. Examples thereof include oleyl myristate, oleyl stearate, and oleyl oleate.
8. Fatty acids having 9 to 22 carbon atoms. Suitable examples include pelargonic, lauric, myristic, palmitic, stearic, isostearic, hydroxystearic, oleic, linoleic, ricinoleic, arachidonic, behenic, and erucic acids.
9. Fatty alcohols having 10 to 22 carbon atoms. Lauryl, myristyl, cetyl, hexadecyl, stearyl, isostearyl, hydroxystearyl, oleyl, ricinoleyl, behenyl, erucyl, and 2-octyl dodecyl alcohols are examples of suitable fatty alcohols.
10. Fatty alcohol ethers. Ethoxylated fatty alcohols of 10 to 20 carbon atoms include the lauryl, cetyl, stearyl, isostearyl, oleyl, and cholesterol alcohols having attached thereto from 1 to 50 ethylene oxide groups or 1 to 50 propylene oxide groups, or a mixture thereof.
11. Ether-esters such as fatty acid esters of ethoxylated fatty alcohols.
12. Lanolin and its derivatives. Lanolin, lanolin oil, lanolin wax, lanolin alcohols, lanolin fatty acids, isopropyl lanolate, ethoxylated lanolin, ethoxylated lanolin alcohols, ethoxylated cholesterol, propoxylated lanolin alcohols, acetylated lanolin, acetylated lanolin alcohols, lanolin alcohols linoleate, lanolin alcohols ricinoleate, acetate of lanolin alcohols ricinoleate, acetate of ethoxylated alcohols-esters, hydrogenolysis of lanolin, ethoxylated hydrogenated lanolin, ethoxylated sorbitol lanolin, and liquid and semisolid lanolin absorption bases are illustrative of emollients derived from lanolin.
13. Polyhydric alcohols and polyether derivatives. Propylene glycol, dipropylene glycol, polypropylene glycol (M.W. 2000-4000), polyoxyethylene polyoxypropylene glycols, polyoxypropylene polyoxyethylene glycols, glycerol, ethoxylated glycerol, propoxylated glycerol, sorbitol, ethoxylated sorbitol, hydroxypropyl sorbitol, polyethylene glycol (M.W. 200-6000), methoxy polyethylene glycols, poly(ethylene oxide) homopolymers (M.W. 100,000-5,000,000), polyalkylene glycols and derivatives, hexylene glycol (2-methyl-2,4-pentanediol), 1,3-butylene glycol, 1,2,6-hexanetriol, ethohexadiol USP (2-ethyl-1,3-hexanediol), C₁₅-C₁₈ vicinal glycol, and polyoxypropylene derivatives of trimethylolpropane are examples thereof.
14. Polyhydric alcohol esters. Ethylene glycol mono- and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol (M.W. 200-6000) mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol 2000 monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene propylene glycol monostearate, glycetyl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters.
15. Wax esters, such as beeswax, spermaceti, myristyl myristate, stearyl stearate.
16. Beeswax derivatives, e.g., polyoxyethylene sorbitol beeswax. These are reaction products of beeswax with ethoxylated sorbitol of varying ethylene oxide content, forming a mixture of ether-esters.
17. Vegetable waxes including carnauba and candelilla waxes.
18. Phospholipids, such as lecithin and derivatives.
19. Sterols. Cholesterol, cholesterol fatty acid esters are examples thereof.
20. Amides, such as fatty acid amides, ethoxylated fatty acid amides, solid fatty acid alkanolamides.
- The lotions further comprise from about 1% to about 10%, preferably from about 2% to about 5%, of an emulsifier. The emulsifiers can be nonionic, anionic or cationic. Examples of satisfactory nonionic emulsifiers include fatty acid alcohols having 10 to 20 carbon atoms, fatty alcohols having 10 to 20 carbon atoms condensed with 2 to 20 moles of ethylene oxide or propylene oxide, alkyl phenols with 6 to 12 carbon atoms in the alkyl chain condensed with 2 to 20 moles of ethylene oxide, mono- and di-fatty acid esters of ethylene oxide, mono- and di-fatty acid esters of ethylene glycol wherein the fatty acid moiety contains from 10 to 20 carbon atoms, diethylene glycol, polyethylene glycols of molecular weight 200 to 6000, propylene glycols of molecular weight 200 to 3000, glycerol, sorbitol, polyoxyethylene sorbitol, polyoxyethylene sorbitan and hydrophilic wax esters. Suitable anionic emulsifiers include the fatty acid soaps, e.g. sodium, potassium and triethanolamine soaps, wherein the fatty acid moiety contains from 10 to 20 carbon atoms. Other suitable anionic emulsifiers include the alkali metal, ammonium or substituted ammonium alkyl sulfates, alkyl arylsulfonates, and alkyl ethoxy ether sulfonates having 10 to 30 carbon atoms in the alkyl moiety. The alkyl ethoxy ether sulfonates contain from 1 to 50 ethylene oxide units. However, it is recognized that certain anionic emulsifiers can result

in a turbid formulation, and hence, anionic emulsifiers are less preferred for use herein.

The balance of the lotion is water or a C₂ or C₃ alcohol, or a mixture of water and the alcohol. The lotions are formulated by simply admixing all of the components together. Preferably the monoalkyl phosphate salt is dissolved in the mixture. Conventional optional components can be included. One such additive is a thickening agent at a level from about 1% to about 10% of the composition. Examples of suitable thickening agents include: cross-linked carboxypolyethylene polymers (sufficiently neutralized), magnesium aluminum silicate, carboxymethylcellulose, hydroxyethylcellulose, acrylic acid polymers (e.g., Acrysol ICS-I, available from Rohm & Haas Corporation), polyethylene glycols, gum tragacanth, gum kharaya, xanthan gums and bentonite. Cationic polymers, such as cationic guar gum, are not preferred for use herein.

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2. Creams.

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Compositions of the present invention also can be formulated in a cream form. The creams comprise safe and effective amounts of the monoalkyl phosphate salt and alkyl amine oxide; from about 0.1% to 95%, preferably from about 10% to about 25%, of an emollient; the balance being water. The emollients above described can also be used in the cream compositions. Optionally, the cream form contains a suitable emulsifier, as previously described. When an emulsifier is included, it is in the composition at a level from about 3% to about 50%, preferably from about 5% to about 20%.

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3. Solutions.

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The compositions of this invention can also be formulated as a solution. The solution form comprises a safe and effective amount of the surfactant composition containing the monoalkyl phosphate salt and amine oxide, usually at least about 0.01% up to about 50% and preferably about 0.1% to about 10%; the balance being water or a suitable organic solvent. Suitable organic materials useful as the solvent or a part of a solvent system are as follows: propylene glycol, polyethylene glycol (M.W. 200-1000), polypropylene glycol (M.W. 425-2025), butylene glycol, glycerine, sorbitol esters, 1,2,6-hexanetriol, ethanol, isopropanol, diethyl tartrate, butanediol, and mixtures thereof.

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These solutions can be applied to the skin as is, or else can be formulated into, for example, squeeze devices as described below or as an aerosol and sprayed onto the skin from an aerosol container, or as a mouth-wash composition and used as an oral rinse. The aerosol compositions further comprise from about 25% to about 80%, preferably from about 30% to about 50%, of suitable propellants. Examples of such propellants are the chlorinated, fluorinated and chlorofluorinated lower molecular weight hydrocarbons. Nitrous oxide, carbon dioxide, butane, and propane can also be used as propellant gases. These propellants are used at a level sufficient to expel the contents of the container.

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Squeeze foamer packages are well known as exemplified by the disclosures in the following patents that are incorporated herein by reference. U.S. Pat. Nos. 3,709,437, Wright, issued Jan. 9, 1973; 3,937,364, Wright, issued Feb. 10, 1976; 4,022,351, Wright, issued May 10, 1977; 4,147,306, Bennett, issued Apr. 3, 1979; 4,184,615, Wright, issued Jan. 22, 1980; 4,598,862, Rice, issued July 8, 1986; and 4,615,467, Grogan et al., issued Oct. 7, 1986; and French Pat. 2,604,622, Verhulst, published Apr. 8, 1988.

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The above containers (packages) do not use any propellant and are therefore safe for the consumer and the environment. They create a foam from almost any surfactant composition. Although there is no need to add foam boosters merely for the purpose of stabilizing the foam, such materials can be desirable. In some compositions the use of foam boosters can even be counterproductive since the foam has to break in order for the container to work properly. The composition is placed in the container reservoir (plastic squeeze bottle). Squeezing the container with the hand forces the composition through a foamer head, or other foam producing means, where the composition is mixed with air and then through a homogenizing means that makes the foam more homogeneous and controls the consistency of the foam. The foam is then discharged as a uniform, non-pressurized aerated foam.

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The minimum pressure to activate the squeeze foamer is about 1 psig, typically from about 2 psig to about 7 psig. The minimum pressure is related to the size of the channels in the dispenser, the viscosity of the composition, etc.

In general, the density of the foam should be between about 0.002 and about 0.25 g/cc, preferably between about 0.01 and about 0.12 g/cc, and more preferably between about 0.02 and about 0.07 g/cc.

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The carrier liquid in a mouthwash is generally a mixture of ethanol and water. The amount of ethanol is generally from about 5% to about 60%, preferably from about 5% to about 25% by weight of the carrier. Water then constitutes the remainder of the carrier liquid mixture. These mouthwash compositions can also contain other optional components such as emulsifying agents as previously described, flavoring agents, sweeteners,

and humectants. Other mouthwash formulations and methods for making mouthwashes useful in the present invention are disclosed in U.S. Patent 4,323,551 to Parran, issued April 6, 1982, which is incorporated by reference herein.

.5 4. Gels.

Compositions herein can be formulated into a gel form by simply admixing a suitable thickening agent to the previously described solution compositions. Examples of suitable thickening agents have been previously described with respect to the lotions.

10 The gelled compositions comprise a safe and effective amount of the surfactant composition, from about 0.5% to about 20%, preferably from about 1% to about 10%, of the thickening agent; the balance being water or a mixture of water and ethanol and propanol.

15 5. Solids.

The compositions of this invention can also be formulated in a solid form, e.g., a stick-type composition. Such compositions comprise a safe and effective amount of the surfactant composition and from about 0.01% to about 99%, preferably from about 60% to about 90%, of the previously described emollients. This composition can further comprise from about 0.1% to about 20%, preferably from about 5% to about 15%, of a suitable thickening agent, and optionally emulsifiers and water. Thickening agents previously described with respect to lotions are also suitable herein.

25 6. Soaps.

The compositions of this invention can also be formulated into a liquid or solid (e.g., bar) soap matrix. Such compositions comprise a safe and effective amount of the surfactant composition ranging from about 0.1% to about 99%; and from about 1% to about 99% of an excipient such as those previously described. Optionally, the soap contains a suitable emulsifier as previously described. When an emulsifier is included, it is in the composition at a level from about 10% to about 50%.

30 7. Dentifrices.

The compositions of this invention can also be formulated as dentifrices. Such dentifrices, especially toothpaste, comprise a safe and effective amount of the surfactant composition ranging from about 0.1% to about 20% by weight of the composition. Toothpaste compositions conventionally contain abrasive materials, sudsing agents, binders, humectants, flavoring and sweetening agents. Suitable dentifrice compositions and the methods of their manufacture useful in the present invention are fully set forth in U.S. Patent 3,535,421 to Briner et al., issued October 20, 1970, which is incorporated by reference herein.

40 8. Shampoos.

Compositions of this invention also can be formulated in a shampoo form. The shampoos comprise a safe and effective amount of the surfactant composition ranging from about 0.1% to about 99%; from about 5% to about 60% of a synthetic surfactant; and the balance water. A secondary surfactant can also be utilized, however, such secondary surfactant should be neutralized by a diamine as described above.

45 These shampoos can contain a variety of nonessential optional components. Such conventional optional ingredients are well known to those skilled in the art, e.g., preservatives, such as benzyl alcohol, ethyl paraben, propyl paraben and imidazolidinyl urea; cationic surfactants, such as cetyl trimethyl ammonium chloride, stearyldimethyl benzyl ammonium chloride, and di(partially hydrogenated tallow) dimethylammonium chloride; thickeners and viscosity modifiers such as diethanolamide of a long-chain fatty acid (e.g. PEG 3 lauramide), block polymers of ethylene oxide and propylene oxide, sodium chloride, sodium sulfate, polyvinyl alcohol, and ethyl alcohol; pH adjusting agents, such as citric acid, succinic acid, phosphoric acid, sodium carbonate; perfumes; dyes; and, sequestering agents, such as disodium ethylenediaminetetraacetate. Such agents generally are used individually at a level of from about 0.01% to about 10%, preferably from about 0.5% to about 5.0% by weight of the composition.

55 Additional minor components can be added to the compositions of this invention in order to increase their attractiveness, versatility, and shelf-life. Perfumes and water soluble, pharmaceutically acceptable dyes or food colors can be added to enhance the attractiveness of these compositions. Antifungal and antimicrobial agents

are useful in preventing mold or bacterial contamination and in increasing the shelf-life of the compositions. Conventional antibacterial agents can be included in the present compositions at levels of from about 0.1% to about 4%, preferably from about 0.2% to about 1%. Typical antibacterial agents which are suitable for use herein are 3,4-di- and 3,4',5-tribromosalicylanilides; 4,4'-dichloro-3-(trifluoromethyl)carbanilide; 3,4,4'-trichlorocarbanilide; phenoxy ethanol or propanol; chlorhexidine salts; hexamidin salts; Irgasan DP 300 (Triclosan); salicylic acid; parachlorometaxylenol; Octopirox; and mixtures of these materials. For general purposes skin cleansing compositions having a pH range from about 5.0 to about 8.0 are desirable. If necessary, the pH of these compositions can be adjusted downward using citric or lactic acid. For skin cleansers which deal with more sensitive skin surfaces, such as in vaginal and perianal cleansers, a pH of about 6.5 is desirable. These and other minor modifications can be made without materially altering or departing from the basic concept of this invention.

The nature of the foam produced determines the usefulness of the present compositions. In order for a foam to be useful as a skin cleansing agent, it must have a uniform consistency, good spreadability, and good cleansing ability.

The foamability and wettability characteristics are governed by the surface tension of the skin cleansing composition. The surface tension for the compositions of this invention varies from about 20 to 70 dynes/cm. For general skin cleansing compositions a range of from about 23 to about 50 dynes/cm is preferred. Liquid compositions having a surface tension in the lower portion of this range possess greater spreading and better wetting characteristics with increased foamability. Foamable compositions having higher surface tensions generally provide more stable foams but are also more difficult to cause to foam and require more force to extrude the foam.

The foam-producing skin cleansing compositions of this invention are particularly advantageous in that they leave a minimum amount of surfactant residue on the surface of the skin. This has been achieved in part by utilizing a low percentage of total surfactants in the skin cleansing compositions itself, and by preparing foams with unusually low density. The present compositions provide foam densities provide good cleansing ability and more importantly, leave a negligible amount of surfactant residue on the surface of the skin upon rinsing or flattening, thereby preserving skin elasticity, and reducing transepidermal moisture loss.

The cleansing ability of these aerated foams is a direct function of the cleansing ability of the surfactant solution itself which produces the foam.

The following non-limiting examples illustrate embodiments of the subject invention wherein both essential and optional ingredients are combined. It is to be understood that these examples are for illustrative purposes only and are not to be construed as limiting the scope of the invention thereto.

EXAMPLE I

A facial cleansing composition for topical administration is prepared by combining the following ingredients:

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	<u>Ingredients</u>	<u>Percent w/w</u>
5	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate	2.500
	Butylene Glycol	2.500
	Methylparaben	0.250
10	Propylparaben	0.150
	Cocoamidopropyldimethylamine oxide ¹	0.150
	Potassium coco(hydrolysed animal protein) ²	0.032
	Glycerin	2.000
15	Aloe Vera	0.500
	Fragrance	0.050
	Color	0.170
20	Xanthan gum ³	0.050
	Water	q.s.

¹ Available as Standamox CAW from Henkel Corporation

² Available as Lamepon 5 from Henkel Corporation

³ Available as Keltrol T from Kelco Corporation

The N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate is formed by heating 1 mole of monolauryl phosphate acid over a steam bath to about 50°C until molten. 1 mole of N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine (available as Quadrol from BASF Corporation) is heated in a separate beaker to 50°C until pourable.

The molten phosphate is slowly added to the N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine. The phosphate is added until a pH of 5.0 to 9.0 is reached (preferably 7.0). The resulting N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate is then cooled to form a clear, yellow solid. The remaining ingredients are then combined in order to produce a facial cleansing composition.

Application of approximately 0.5 grams to the skin will provide a foaming cleanser possessing good cleansing power and detergency, which is mild and non-irritating, and leaves little, if any, residual film remaining on the cleansed surface of the skin.

Substantially similar results are obtained when the monolauryl phosphate acid is replaced with an equivalent amount of monococoylphosphate acid, monolaurylphosphate acid, monoisostearylphosphate acid, mono-stearylphosphate acid, monomyristylphosphate acid, monooleoylphosphate acid, monopalmitylphosphate acid, monocaprylphosphate acid, monoundecylenylphosphate acid, monotridecylphosphate acid, mono(methylmyristyl)phosphate acid, mono(isopropylauryl)phosphate acid, mono(isodecylneopentyl)phosphate acid, monocetylphosphate acid, and mono(isopropylmyristyl)phosphate acid and mixtures thereof.

EXAMPLE II

A facial cleansing composition for topical administration is prepared by combining the following ingredients:

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	<u>Ingredients</u>	<u>Percent w/w</u>
5	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate	27.000
	Lauric acid	4.000
10	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine ¹	2.000
	Cocoamidopropyltrimethylamine oxide	4.000
	Carboxyvinyl polymer ²	0.200
	Glycerine	8.000
15	Sorbitol	2.000
	Water	q.s.

¹ Available as Quadrol from BASF-Wyandotte

² Available as Carbopol 941 from B.F. Goodrich Company

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EXAMPLE III

A facial cleansing compositions for topical administration is prepared by combining the following ingredients:

	<u>Ingredients</u>	<u>Percent w/w</u>
30	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate	3.000
	Lauric acid	1.000
35	Cocoamidopropyltrimethylamine oxide	0.500
	Potassium coco(hydrolysed animal protein)	0.500
	Hydroxyethyl cellulose	2.000
40	Methyl paraben	0.100
	Propyl paraben	0.100
	Glycerin	3.000
	Fragrance	0.100
45	Color	0.001
	Water	q.s.

EXAMPLE IV

50 A facial cleansing gel composition for topical administration is prepared by combining the following ingredients:

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	<u>Ingredients</u>	<u>Percent w/w</u>
5	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate	10.000
	Cocoamidopropyltrimethylamine oxide	2.000
	Acrylic acid polymer	0.500
10	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine	1.000
	Glycerin	5.000
	Lauric acid	2.000
15	Water	q.s.

EXAMPLE V

20 A facial shaving foam composition for topical administration is prepared by combining the following ingredients:

	<u>Ingredients</u>	<u>Percent w/w</u>
25	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monolaurylphosphate	7.000
	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine monopalmityl phosphate	7.000
30	Lauric acid	1.500
	Palmityl acid	1.500
	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine	2.000
35	Cocoamidopropyltrimethylamine oxide	2.000
	Fragrance	0.100
	Aloe Vera	2.000
40	Water	q.s.

EXAMPLE VI

45 A facial cleansing composition for topical administration is prepared by combining the following ingredients:

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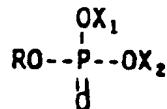
	<u>Ingredients</u>	<u>Percent w/w</u>
5	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine (1 mole ethyloxylated) monolaurylphosphate	27.000
	Lauric acid	4.000
10	N,N,N',N'-tetrakis(2-hydroxypropyl)-ethylenediamine ¹	2.000
	Cocoamidopropyltrimethylamine oxide	4.000
	Carboxyvinyl polymer ²	0.200
15	Glycerine	8.000
	Sorbitol	2.000
	Water	q.s.

¹ Available as Quadrol from BASF-Wyandotte

20 ² Available as Carbopol 941 from B.F. Goodrich Company

25 **Claims**

1. A surfactant composition comprising:
 (a) from about 0.1% to about 99.0% of one or more of a surfactant compound of the formula:



35 wherein R is a hydrophobic group or the condensation product of a hydrophobic group with ethylene oxide, and wherein X₁ and X₂ are independently selected from the group consisting of hydrogen, alkali metal, ammonium, substituted ammonium and alkylene diamine, provided that at least one of X₁ and X₂ is an alkylene diamine; and

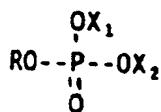
40 (b) from about 0.1% to about 20.0% of one or more of an alkylamine oxide which has a hydrocarbon group having from about 10 to about 14 carbon atoms.

2. A compound according to Claim 1 wherein R is alkyl or alkenyl having an average of from about 10 to about 18 carbon atoms.
- 45 3. A compound according to Claim 2 wherein R is alkyl or alkenyl having an average of from about 10 to 14 carbon atoms, wherein said substituted ammonium is selected from the group consisting of alkoxyLATED ammonium, alkylammonium, alkoxyLATED aliphatic amines and polyethoxylated amines, and wherein said alkali metal is selected from the group consisting of sodium, potassium and lithium and mixtures thereof.
- 50 4. A compound according to Claim 3 wherein said alkylammonium is selected from the group consisting of trimethylammonium, triethylammonium, dibutylammonium, butyldimethylammonium, isopropyl-dimethylammonium, diglycolamines, glucamines and mixtures thereof and wherein said substituted alkylammonium is a hydroxyalkylammonium.
- 55 5. A compound according to Claim 4 wherein at least one of X₁ and X₂ is a totally hydroxyalkylated alkylene diamine and wherein R is the condensation product of a hydrophobic group with from about 1 to about 10 moles of ethylene oxide.

6. A compound according to Claim 5 wherein at least one of X₁ and X₂ is an alkylene diamine wherein the alkylene moiety contains from 2 to about 6 carbon atoms, said alkylene diamine having been oxyalkylated with an alkylene oxide containing at least 2 carbon atoms or a mixture of alkylene oxides containing from 2 or more carbon atoms.
- 5 7. A compound according to Claim 6 wherein at least one of X₁ and X₂ is N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.
- 10 8. A detergent composition according to Claim 7 in a form selected from the group consisting of soaps, creams, solutions, mouthwashes, dentifrices or shampoos.
9. A detergent composition according to Claim 1 comprising a mixture of the diamine monoalkyl phosphate salts wherein R is selected from the group consisting of C₁₂ to C₁₄ alkyl or alkenyl and C₁₆ to C₁₈ alkyl or alkenyl and wherein said salts are present in a ratio of from about 60:40 to about 40:60.
- 15 10. A detergent composition according to Claim 1 comprising a mixture of the diamine monoalkyl phosphate salts wherein R is selected from the group consisting of the condensation product of a C₁₂ to C₁₄ alkyl or alkenyl with from about 1 to about 10 moles of ethylene oxide and the condensation product of a C₁₆ to C₁₈ alkyl or alkenyl with from about 1 to about 10 moles of ethylene oxide and wherein said salts are present 20 in a ratio of from about 60:40 to about 40:60.
11. A detergent composition having low irritation effect comprising:

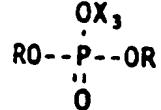
- (a) from about 0.1% to about 99% of a surfactant component comprising:

(i) one or more of a surfactant compound having the formula:



30 wherein R is a hydrophobic group or the condensation product of a hydrophobic group with ethylene oxide, and wherein X₁ and X₂ are independently selected from the group consisting of hydrogen, alkali metal, ammonium, substituted ammonium and alkylene diamine, provided that at least one of X₁ and X₂ is an alkylene diamine; and

35 (ii) one or more of a surfactant compound having the formula



40 wherein R is a hydrophobic group or the condensation product of a hydrophobic group with ethylene oxide, and wherein X₃ is selected from the group consisting of hydrogen, alkali metal, ammonium, substituted ammonium and alkylene diamine;

45 wherein the ratio of (i) to (ii) is from about 99:1 to about 70:30; and

(b) from about 0.1% to about 20.0% of one or more of an alkylamine oxide which has a hydrocarbon group having from about 10 to about 14 carbon atoms.

- 50 12. A detergent composition according to Claim 11 wherein R is alkyl or alkenyl having an average of from about 10 to 18 carbon atoms and wherein said substituted ammonium is selected from the group consisting of alkoxyLATED ammonium, alkylammonium, alkoxyLATED aliphatic amines and polyethoxylated amines.
13. A detergent composition according to Claim 12 wherein at least one of X₁ and X₂ is N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.
- 55 14. A detergent composition according to Claim 13 wherein R is alkyl or alkenyl having an average of from about 10 to about 14 carbon atoms.

15. A detergent composition according to Claim 13 where in R is the condensation product of an alkyl or alkenyl having an average of from about 10 to about 14 carbon atoms with from about 1 to about 10 moles of ethylene oxide.
- 5 16. A detergent composition according to Claim 13 in a form selected from the group consisting of soaps, creams, solutions, mouthwashes, dentifrices or shampoos.
17. A detergent composition according to Claim 15 in a form selected from the group consisting of soaps, creams, solutions, mouthwashes, dentifrices or shampoos.

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(54) **Surfactant compositions.**

(57) Disclosed are novel low skin irritation surfactant compositions which are high in foaming properties containing, as active ingredients, a diamine monoalkyl phosphate salt and an alkylamine oxide.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number ..

EP 91 30 2461

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
A	EP-A-0 077 920 (KAO CORP.) * Page 3, paragraph 2; page 6(C); page 9, paragraph 1; page 19, table 3 *	1,11	C 11 D 1/83 C 11 D 1/34 C 11 D 1/75						
A	EP-A-0 081 801 (KAO CORP.) * Pages 3,6; page 11, examples 2,3; page 10, example 1; claim 1 *	1,11	A 61 K 7/08						
A	EP-A-0 279 457 (KAO CORP.) * Page 5; page 9, table 3 *	1,11							
A	EP-A-0 210 704 (THE PROCTER AND GAMBLE CO.) * Page 4; examples *	1,11							
D,A	US-A-4 290 904 (M.H. POPPER) * Whole document *	1,11							
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)						
			C 11 D A 61 K						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>11-10-1991</td> <td>GOLLER P.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	11-10-1991	GOLLER P.
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